Atmos. Chem. Phys. Discuss., 12, C7888–C7890, 2012
www.atmos-chem-phys-discuss.net/12/C7888/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Extreme ^{13}C depletion of CCl_2F_2 in firn air samples from NEEM, Greenland" *by* A. Zuiderweg et al.

Anonymous Referee #5

Received and published: 9 October 2012

This paper presents the first firn air measurements of the stable carbon isotope ratio d13C in CFC-12. The d13C measurements show extreme depletion at depth. Using a firn air model, this is interpreted to imply even larger depletion in atmospheric values around 1950. Mass balance calculations show that this must be due to changes in the isotopic composition of the emissions.

The paper is generally well written and the results appear robust. The study is particularly of interest because this is something that hasn't previously been measured in firn, so this is the first atmospheric reconstruction of C13 in CFC-12. It is not so clear what the estimate of the variation of the isotopic composition of emissions could tell us about the budget of CFC-12 (e.g., if we knew the isotopic composition of the emissions due to different production methods or uses, would this improve estimates of emis-

sions or their delayed release due to leakage?). However, it is still an interesting result that deserves publication. I have some minor suggestions that might help improve the manuscript.

page 18501, line 15-17 - I would recommend deleting the last sentence of the abstract, about propagating into the future. Certainly it could be mentioned in the paper, but I don't believe that it is an important result that deserves mention in the abstract. Isotopes are used here to understand the processes in the CFC-12 budget, their future behavior only matters in this context, and not in its own right. Deleting the sentence would avoid the possibility that a reader could think that there is anything significant about the future levels of 13C in CFC-12.

page 18503, line 20 - Why "unusually". What is usual? Perhaps "unexpectedly" would be a better word, or nothing.

Page 18504, line 22 - You could specify here whether the FASD was expanded with air from the firn hole or the atmosphere.

Page 18508, Section 3.2 - what values of the diffusion coefficients were used for CFC-12 and 13C in CFC12?

page 18511, line 5 - You could mention that although Buizert et al 2012 showed a significant range between models in the calculated diffusive fractionation for d13CO2 at depth, that because the magnitude of the diffusive fractionation in 13C in CFC-12 is so small compared to the variation measured in the firn, the uncertainty in parameterisation of lock-in zone diffusion is not important here.

Page 18512, line 17 - rather than "epsilon is estimated at -35 permil", you should put "epsilon is assumed to be -35 permil", to be clear that it is deltaP that you are estimating with this calculation, not epsilon.

Page 18513, line 4 - add "to estimate deltaP" at the end of the sentence, after 2000. This will help make it very clear for the reader what you are estimating.

Sapart et al 2012 is mentioned in the text but is not listed in the references.

You could give the equation for the best case 3rd order polynomial, in case someone in the future would like to compare it to new reconstructions of 13C in CFC-12 from archived air or firn.

Can you rule out fractionation during collection of firn air as a possible cause of the depletion?

Fig 3 - I recommend adding the profile of CFC-12 from the firn model calculated with the atmospheric scenario from Buizert et al, instead of the lines between symbols, noting the instrument and calibration error described on page 18507. Although the match might not be perfect, this would demonstrate general consistency with the atmospheric scenario (and therefore the NEEM 2008 campaign).

Fig 4 - As in Fig 3, rather than the line between points, you could show the firn model profile of d13C for the best case, either the 3rd or 4th degree polynomial. Just one case, not the envelope as in Fig 5.

Fig 6 - Add "atmospheric" after "Reconstructed".

Fig 7 - Make the symbols clearer, it is hard to see them. Perhaps filled symbols would be better.

Fig 8 - Could you split the contributions of fractionation into diffusion and gravitation? This would be useful for comparison with other estimates of these quantities, particularly as they partly cancel each other.

Fig 9 - In the legend, specify which of these refer to the atmosphere and which to the emissions.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 18499, 2012.